A GRAND CANONICAL MONTE-CARLO STUDY OF H₂ ADSORPTION IN PRISTINE AND Li-DOPED CARBON REPLICAES OF FAUJASITE ZEOLITE

Thomas Roussel, Roland J.-M. Pellenq, Christophe Bichara

CRMC-N – CNRS, Campus de Luminy, 13288 Marseille, cedex 09, France.

Email: pellenq@crmcn.univ-mrs.fr

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Abstract

The first step of this work was to generate using atomistic simulation, a porous carbon material with an ordered pore network using the faujasite Y zeolite as a templating matrix. For this purpose, we used the Grand Canonical Monte-Carlo (GCMC) technique in which the carbon-carbon interactions were described with reactive bond-order potential assuming the carbon-zeolite interactions to be relevant to physisorption. The intrinsic stability of the nanoporous carbon material was then investigated. We also performed a structural analysis of the resulting carbon porous structure including the determination of the pore size distribution. Such a new carbon form has a very ordered porous structure that can be used as a model adsorbent to validate adsorption theory and characterization methods. At a second stage, we calculated for these pristine structures, hydrogen adsorption isotherms at different temperatures with the GCMC technique using ab initio adsorbate-carbon interaction potentials. Although our carbon replicas have an optimum pore size for H₂ docking, we demonstrated that they cannot be used as for an efficient storage at room temperature under 300 bars. By contrast, when doped with lithium (LiC₆), we found, that room temperature H₂ storing become possible: we obtain 4% in weight (37 kg/m³) under 300 bars. The origin of these good storing performances is to be found at the atomistic level thanks to the Li to C electron transfer.

Introduction

Microporous carbon materials are interesting for several applications such as hydrogen storage, catalysis or electrical double layer capacitors. The development of the negative templating method to obtain carbon replicas from ordered templates, has lead to the synthesis of several new materials which have interesting textural properties, attractive for energy storage. Among the possible templates, zeolites can be used to obtain ordered carbon materials with very high microporous volumes. Experimental results for carbon zeolite-templated nanostructures can be found in a series of papers; see for instance ref. [Wang et al 2000, Ma et al 2002]. For instance carbon replica of faujasite zeolite is an ordered porous carbon structure that forms a 3D network made of ~10 Å cages connected to each other through 7 Å large windows that can be an interesting medium for storing hydrogen. In this paper, we present the results of GCMC simulations of carbon adsorption in the porosity of the siliceous faujasite zeolite framework. We first analyse the resulting carbon structure and at a second stage, present H₂ adsorption results in the pristine and lithium doped version of this new material.

Computational methods

The carbon-zeolite potential energy

The interactions of carbon with Si, and O atoms of the Y framework is assumed to remain weak, i.e. in the physisorption energy range. This is the reason why we have used a PN-TrAZ potential function as originally reported for adsorption of rare gases and nitrogen in silicalite-1 [Pellenq et al, 1994]. The PN-TrAZ potential function is based on the usual partition of the adsorption intermolecular energy restricted to two body terms only. In the TrAZ model, the interaction energy (uᵢ) of a (neutral) carbon atom at position i with the zeolite species, is given by:

\[ uᵢ = \sum_{j≠(i,n)} Aᵢ j e^{-β_{ij}} - \sum_{n=1}^{r} f_n \left( \frac{C_{2n,j}}{r_{jn}^n} \right) - \frac{1}{2} aE_i^2 \]  

(1)
The sum runs over all atomic sites in the matrix that are oxygen, aluminium sodium and silicon atoms of faujasite. A detailed description of this adsorption potential and parameters are given in Table 1.

<table>
<thead>
<tr>
<th>C-Si</th>
<th>C-O</th>
<th>Faujasite partial charges</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆ (E₆a₀⁶)</td>
<td>13.156</td>
<td>36.580</td>
</tr>
<tr>
<td>C₈ (E₈a₀⁸)</td>
<td>257.28</td>
<td>834.82</td>
</tr>
<tr>
<td>C₁₀ (E₁₀a₀¹⁰)</td>
<td>—</td>
<td>20100</td>
</tr>
<tr>
<td>A(E₆)</td>
<td>468.952</td>
<td>234.681</td>
</tr>
<tr>
<td>b(a₀⁻¹)</td>
<td>1.975</td>
<td>1.944</td>
</tr>
</tbody>
</table>

Table 1: PN-TraZ potential parameters for simulating carbon in Faujasite zeolite

**The carbon-carbon interactions**

The interaction between the carbon atoms is modeled using the REBO potential [Brenner, 1990]. The REBO potential takes into account the chemical bonding between the carbon atoms depending on the local environment of each carbon atom.

**Simulation technique to obtain a carbon replica**

We performed standard Grand Canonical Monte-Carlo simulations [Pellenq et al., 1995] on a periodic box containing a number of zeolite unit cells. Starting with a C₂ dimer, we gradually raised the chemical potential and recorded the average number of adsorbed carbon atoms. This allowed us to calculate carbon adsorption isotherms. Note that the chemical potential of the carbon atoms is referred to that of a fictitious monoatomic ideal gas. Hence we are not simulating the real experimental process that is based on the impregnation and carbonization of organic precursors as furfurylic alcohol [C.Vix-Gutterl et al., 2002]. A minimum of 5.10⁵ Monte Carlo macro-steps was performed, each macro-step consisting of randomly performing 1000 attempted placements, 10 attempted insertion and 10 attempted removals of an adsorbate atom. We stored the adsorbate/substrate interaction on a 3D grid (step: 0.2 Å). The adsorbate/substrate energy is then obtained by an interpolation procedure of the 3D energy grid. This procedure avoids direct summation over the matrix species in GCMC runs.

**The hydrogen-carbon, hydrogen-hydrogen and hydrogen-lithium interactions**

To simulate the adsorption of hydrogen in the pure carbon replica, we used a Lennard-Jones potential function parameterized in the case of adsorption of H₂ on graphite. The hydrogen-hydrogen interactions were also described with a LJ function with parameters adjusted of the bulk liquid hydrogen equation of state. We wish also to consider a doped structure. Using ab initio DFT-B3LYP calculations Maresca et al were the first to demonstrate that doping the carbon skeleton using alkaline elements such as lithium also obtaining a strong physisorption of hydrogen in carboneous substrates [Maresca, 2004]. The underlying mechanism for such a super-physisorption is the creation of a polarization (or induction) term in the hydrogen-(doped) matrix Hamiltonian that is attractive and proportional to the square of the local electric field created by the doped-matrix electric charges in the pore voids that couples with the hydrogen molecule polarizability [Pellenq et al., 1994]. For the sake of simplicity and transferability in the case of the doped system, we retain the LJ form and parameters as they are for the H₂-C interactions in the case of the un-doped matrix and keep the hydrogen molecular polarizability as a disposable parameter. The total H₂-Li-doped carbon system potential function is thus:

\[
\begin{align*}
V_{H_2}^{tot} = 4\pi \sum_{(H_2/Li/C)} \left\{ \frac{\epsilon_{H_2}(H_2/Li/C)}{r_{H_2}^{6}} - \frac{\sigma_{H_2}(H_2/Li/C)}{r_{H_2}^{12}} \right\} + \left( - \frac{\epsilon_{H_2}(H_2/Li/C)}{r_{H_2}^{6}} + \frac{\sigma_{H_2}(H_2/Li/C)}{r_{H_2}^{12}} \right) \right\} - \frac{1}{2} \alpha_{H_2}^{\text{Li}} |E|^2
\end{align*}
\]
The molecular hydrogen polarizability is then obtained by adjusting such a potential function on *ab initio* plane-wave DFT-GGA points (ABINIT code) in the case of a (periodic) interface made of two graphene sheets confining a single hydrogen molecule and Li species (LiC₁₂, see Fig 1a). All parameters concerning hydrogen adsorption are given in table 2. It is interesting to note that the partial charge as given by the *ab initio* calculations is 0.7 ě and that the adsorption energy (at minimum see Fig 1) is 15 kJ/mol. Further calculations for the same system but with the LDA approximation give an adsorption energy of 24 kJ/mol. These two values are lower and upper bounds of the DFT-B3LYP calculations that give a H₂ adsorption energy of -21 kJ/mol for a LiC₆ doped system [Maresca *et al.*, 2004].

<table>
<thead>
<tr>
<th></th>
<th>σ (Å)</th>
<th>ε / k (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ – H₂</td>
<td>2.96</td>
<td>34.2</td>
</tr>
<tr>
<td>H₂–C</td>
<td>3.18</td>
<td>30.945</td>
</tr>
<tr>
<td>H₂–Li</td>
<td>2.66</td>
<td>24.76</td>
</tr>
</tbody>
</table>

**Table 2:** potential parameters for GCMC simulation of H₂ adsorption

The loci of Li ions were obtained by energy minimization assuming their *ab initio* charge (see above), the composition (LiC₆) giving the charge (homogenously distributed) of carbon atoms.

**The simulation of hydrogen adsorption in doped/undoped carbon replicas**

We used the Grand Canonical Monte-Carlo technique as described above to simulate the adsorption of molecular hydrogen using the potential function reported above with parameters given in Table 2 for the hydrogen-matrix interactions. Note that the hydrogen-hydrogen parameters were fitted to reproduce the (p,P) equation of state above the critical point. The GCMC simulation runs were performed in a single unit cell of relaxed C-FAU.
Results and discussion

As a test case, we used the GCMC technique to simulate the vapor deposition of carbon in the nanopores of zeolite AlPO4-5. We showed that narrowest single wall nanotube can be synthesized in the cylindrical channel of AlPO4-5 zeolite (pore diameter 7 Å) in agreement with the experimental work of Wang et al [Wang et al, 2000]. We also demonstrated that a zeolite such as silicalite with smaller pores (diameter 5 Å) than AlPO4-5, does not allow obtaining nanotubes but a mesh of intercrossing carbon chains. As shown in Figure 2, carbon adsorption in faujasite at 1000 K leads to the formation of a fully 3D connected porous carbon structure that is the (negative) replica of the original zeolite cavity network. This new form of carbon material is also stable upon matrix removal as shown. A further relaxation step using the molecular dynamics technique in the canonical ensemble (at high temperature) allows obtaining a structure with very few defects and made (nearly) exclusively of bent carbon six-member rings. This final structure has very high mechanical properties. Its calculated bulk modulus is only 5 times smaller than that of diamond; a very interesting result since the C-Y replica has a rather low density of 0.9 g/cc. It is interesting to note that this structure is close to those predicted by Terrones et al using Schwarz minimal curved surfaces [Terrones et al, 2003].

Figure 2: GCMC carbon replica of faujasite Y obtained at T = 1000 K and relaxed in an additional molecular dynamics step at 3000 K.

Figure 3 presents H2 GCMC simulated adsorption isotherm (at 77 K) on the theoretical Y carbon replica (based on standard H2/C and H2/H2 Lennard-Jones parameters given in Table 2) and compares to experimental volumetric data. The agreement between simulation and experiment is satisfactory. Note that we considering data at room temperature, the amount adsorbed considerably decreases (~ 1.8 w% at 300 bar). Although this is a very good value for carbon materials, it should be indicated that this is very close to the value of the bulk equation of state: storing H2 in pure carbon materials at room temperature is not interesting even in materials with optimized pore size and pore distribution such as carbon replica of faujasite zeolite. Figure 4a presents the doped (LiC6) unit cell of carbon replica of faujasite. One can see that Li ions stick on the pore wall letting free the pore core for H2 adsorption. Room temperature H2 adsorption isotherms is presented in Figure 4b along with that of the 77 K data for undoped system as a reference. Clearly, doping induces a larger storage amount. The reason for such an

Figure 3: GCMC H2-adsorption isotherm in C-FAU (red squares). Comparison with experiment [Didion et al 2007] (blue/green triangles)
effect have to be found at an atomistic level. This is an induction (or polarization) effect that corresponds to the second term of H2-doped matrix potential function (see equation 3). In the present case, doping was achieved using a charge transfer process between alkaline species (lithium) and the carbon skeleton. We believe this effect to be quite general: any charge localization in a microporous environment will create strong electric field that in turn will enhance the H2 adsorption energy, a necessary condition to achieve an efficient storage at room temperature.

**Conclusion**

Through a series of different atomistic simulation procedures, we have shown the conditions for an enhanced molecular hydrogen physisorption allowing the storage of a large hydrogen amount at room temperature. The first step was obtaining carbon replica of faujasite by Grand Canonical Monte-Carlo simulation of carbon adsorption in the pore of faujasite zeolite. This procedure allows creating a new form of material is a crystalline porous carbon with well-defined pores. However, even with these optimized pores, we demonstrate that these materials are of no interest for hydrogen storage at room temperature. We believe this conclusion to be general for all carbon materials. We also found that upon doping that achieves electric charge localization on the carbon skeleton, a large hydrogen quantity can be stored in these porous carbons at room temperature. This is a polarization effect that corresponds to the creation of electric fields in the porous voids that couple with hydrogen polarizability hence allowing an enhanced physisorption.

**References**


Didion A, Gadiou R., Vix, C., private communication


